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EVALUATION OF THERMAL AGGLOMERATION FOR FINE PARTICLE CONTROL

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SUMMARY

The agglomeration or growth of fine particles is, in principle, attractive. If large particles can be produced with realistic residence times and energy expenditures, conventional control systems could be used with ease in controlling fine particulate pollutants. This task was undertaken to evaluate the potential of thermal agglomeration in fine particle control.

Both theoretical analyses and experimental studies pinpoint an overriding disadvantage of thermal agglomeration with regard to industrial gas cleaning applications--the long residence time required to achieve significant particle growth. Residence times of the order of many minutes or even hours are required for significant agglomeration and particle growth to occur via thermal agglomeration. In contrast, industrial gas cleaning applications would require residence times of 10 sec or less.

Successful utilization of the factors which promote thermal agglomeration is not likely to reduce residence times to anything near those required for industrial applications. Thus, thermal agglomeration is not a viable approach to pursue for augmenting the ability of control systems to collect fine particulate emissions.

INTRODUCTION

A variety of forces can cause the movement of particles toward one another to produce collisions and subsequent agglomeration. When particles come into contact with each other and agglomerate, strictly as a result of Brownian movement (diffusion), then the process is termed "thermal agglomeration."

If the properties of the particle surfaces are disregarded and the probability of sticking together after collision is assumed to be unity, then the theory of coagulation depends on the mechanics of collision. Based on these assumptions, two approaches have been reported for explaining thermal agglomeration.[1] One is the continuum approach which comes from Smoluchowski's work on the behavior of dispersed systems[2] and the second is the free molecule approach (i.e., gas kinetic theory approach). Each approach is reviewed in the next section. The discussion of theory is followed by a section on experimental studies and another on conclusions.

THEORETICAL ASPECTS OF THERMAL AGGLOMERATION

Based on Smoluchowski's assumption that thermal agglomeration is a diffusion process, Zebel[3] shows that for a general case of particles of different radii

$$\dot{N}_{12} = 4\pi r_{12}^2 D_2 \left(\frac{\partial n}{\partial \bar{r}}\right)_{\bar{r} = r_{12}} \qquad (1)$$

where $\dot{N}_{12}$ is the number of particle 2 with radius r_2, diffusing in unit time to a fixed particle 1 with radius r_1. In Eq. (1), $r_{12} = r_1 + r_2$ and is the distance between the centers of the two particles at the moment of contact; D_2 is the diffusion coefficient for the particles of kind 2 and $n = n(\bar{r}, r_2, t)$ is the concentration of particles of radius r_2 at time t as a function of distance $\bar{r}$ from particle 1.

To determine the concentration gradient $\left(\frac{\partial n}{\partial r}\right)$, the diffusion equation is solved in spherical coordinates using appropriate boundary conditions.[3] This results in

$$\frac{\partial n}{\partial r} = \frac{n(r_2,t)}{r_{12}} \tag{2}$$

Substitution of Eq. (2) into Eq. (1) yields the number of particles of kind 2 diffusing towards and adhering to fixed particle 1 per unit time,

$$\dot{N}_{12} = 4\pi r_{12} D_2 n(r_2,t) \tag{3}$$

Equation (3) assumes particle 1 to be stationary. In reality, due to Brownian movement, particle 1 is also mobile and diffuses with a coefficient D_1. Thus, the total particle flux is given by the following expression

$$\dot{N}_{12} = 4\pi(r_1 + r_2)(D_1 + D_2)n(r_2,t) \tag{4}$$

By expressing the diffusion coefficients in terms of the particle mobility $\phi(\phi = D/kT)$ and introducing the coagulation constant K_o, Eq. (4) can be written as

$$\dot{N}_{12} = K_o(r_1,r_2)n(r_2,t) \tag{5}$$

where $K_o(r_1,r_2) = 4\pi(\phi_1 + \phi_2)(r_1 + r_2)kT$

k = Boltzmann's constant, and

T = absolute temperature

For highly dispersed aerosols the coagulation constant must be corrected for discontinuity in concentration at the surface of the absorbing particle. The correction becomes appreciable when the apparent mean free path of the aerosol particles is comparable with the radius of the absorbing sphere; according to Fuchs[4] this occurs when $r \leq 0.1$ μm and according to Hidy and Brock[5] the cutoff limit is when the Knudsen number is > 0.01. Physically, this means that diffusion equations can be applied to Brownian motion only for time intervals which are large compared with the relaxation time, τ, of the particles or for distances larger than the mean free path of the aerosol particles.

For conditions where the diffusion equations are not applicable, the laws of kinetic gas theory must be used. The kinetic gas theory approach leads to the following equation for $\dot{N}_{12}$

$$\dot{N}_{12} = 4\pi(r_1 + r_2)(D_1 + D_2)n(r_2,t)\left(\frac{1}{1 + G_o}\right) \qquad (6)$$

where $G_o = 4\left(\frac{D_1 + D_2}{r_1 + r_2}\right)\left(\frac{m_1 m_2}{m_1 + m_2} \cdot \frac{\pi}{8kT}\right)^{1/2}$

Equation (6) can be written in the simplified form

$$\dot{N}_{12} = K_o f n(r_2,t) \qquad (7)$$

where K_o = coagulation coefficient and

$$f = \frac{1}{1 + G_o} .$$

The factor, f, represents the gas kinetic correction factor.

Tables 1 and 2 present values of the coagulation constant calculated from diffusion theory and from gas kinetic theory. As shown in Tables 1 and 2, significant differences exist in the values for small particles and only slight differences occur as the particle size reaches 1 μm.

Table 1. VALUE OF THE COAGULATION CONSTANT $K_o(r_1,r_2)(10^{-10}$ cm^3 sec^{-1})[a/]

r_1 (μm)	r_2 (μm) 0.001	0.01	0.1	1.0
0.001	803.4			
0.01	2,232	84		
0.1	20,299	234.3	12.68	
1.0	201,054	2,121	36.69	6.6

a/ Calculated from diffusion theory.

Table 2. THE COAGULATION CONSTANT
$K(r_1,r_2) = K_o f(10^{-10}\ cm^3\ sec^{-1})$ a/

r_1 (μm)	r_2 (μm) 0.001	0.01	0.1	1.0
0.001	8.78			
0.01	180.2	21.0		
0.1	8,845	168.5	11.10	
1.0	178,100	2,032	35.95	6.44

a/ Taking into account the gas kinetic correction, f .

An important observation on the data presented in Tables 1 and 2 is that coagulation coefficients are small. As a result, long times would be required to achieve significant particle growth.

In addition to the rate of coagulation, another important factor is the variation of particle size distribution with time. An equation for the change with time of the size distribution of aerosols due to thermal coagulation is given by Müller.5/

$$\frac{\partial n(m,t)}{\partial t} = \int_0^{m/2} K(m_1,m-m_1)n(m_1,t)n(m-m_1,t)dm_1 - n(m,t)\int_0^{\infty} K(m,m_1)n(m_1,t)dm_1 \ , \qquad (8)$$

where $n(m,t)dm$ is the number of aerosol particles per cubic centimeter at the time t, whose masses lie between the values m and $m + dm$, while $K(m_1,m_2)$ gives the value of the coagulation constant between aerosol particles of the masses m_1 and m_2. The physical meaning of this integro-differential equation is that a particle of mass m can only come into existence if two particles with masses m_1 and $(m-m_1)$ collide: it can be integrated either from $m_1 = 0$ to $m_1 = m/2$ or from $m_1 = 0$ to $m_1 = m$. The integral value must be halved as, otherwise,

each possible combination is counted twice. The second integral expresses the fact that each particle of mass m, disappears from the fraction m to $m + dm$ after colliding with a particle of mass m_1.

Equation (8) requires a computer solution unless simplifying assumptions are made. Figure 1 illustrates a solution to Eq. (8) presented by Zebel[7] starting with a highly peaked particle size distribution. Schumann[8] and Todes[9] have developed asymptotic solutions to Eq. (8). Schumann suggests that Eq. (9) can be used for the case of constant K when $Kn_o t \gg 1$

$$n(m) = \frac{c}{\bar{m}^2} e^{-m/\bar{m}} \tag{9}$$

where c = weight concentration of aerosol,

$$\bar{m} = \frac{c}{n} = \frac{c(1 + 0.5Kn_o t)}{n_o} = \frac{Kct}{2} = \text{mean mass of particle at time } t .$$

By making simpler assumptions Smoluchowski[10,11] obtained, instead of the integro-differential equation, a simple differential equation which is easily solved. If only the concentration of the total number of particles, n, is considered and the same value of K_o, the coagulation constant, is used for all particles, then the fundamental equation of coagulation becomes

$$\frac{dn}{dt} = -\frac{K_o}{2} n^2 \tag{10}$$

The factor $1/2$ is again necessary so that each aggregate should be counted only once. The solution of Eq. (10) is

$$\frac{1}{n} - \frac{1}{n_o} = \frac{K_o}{2} t \quad \text{or} \quad n = \frac{n_o}{1 + \frac{K_o}{2} n_o t} \tag{11}$$

where n_o is the initial particle number concentration at time $t = 0$.

Equation (11) for the particle number concentration as a function of time, t, is a good approximation for the size distributions occurring in many aerosols.

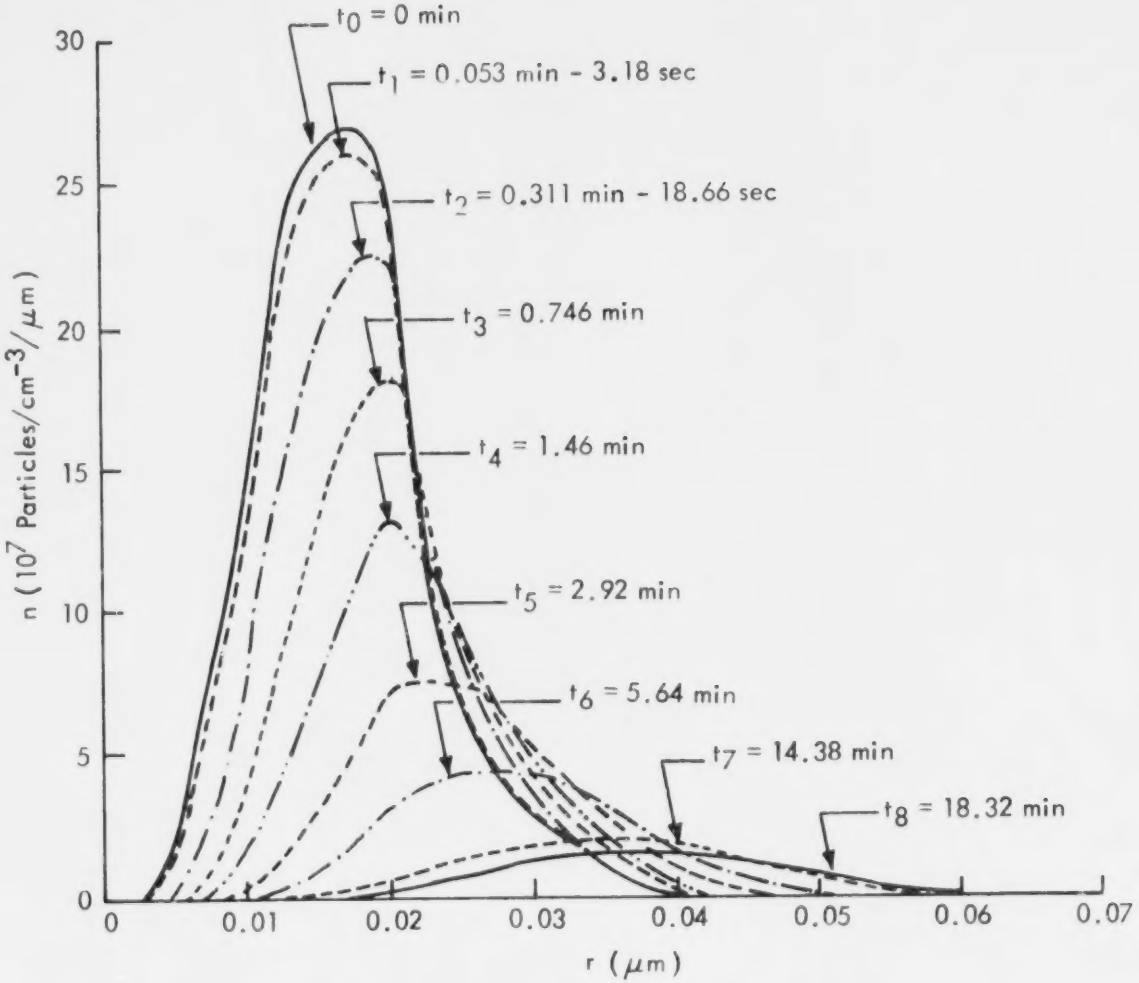

Figure 1. Calculated change in particle size distribution with time.[7]

The preceding theoretical analyses of thermal agglomeration indicate that the main variables influencing the rate of agglomeration are particle concentration, particle size, gas composition, and gas temperature. Thermal agglomeration would be most effective (i.e., occur at the fastest rate) in aerosol systems which have: (a) a high initial grain loading; and (b) a high degree of polydispersity. However, it is clear from the analyses that the rate of thermal agglomeration will be quite slow for aerosols of interest in industrial gas cleaning because the agglomeration coefficient is of the order of 10^{-7} to 10^{-10} cm^3 sec^{-1} for such systems. The long times which would be required to achieve significant particle growth are a severe negative feature with regard to utilization of thermal agglomeration in industrial systems.

Experimental studies on thermal agglomeration of aerosols generally support the predictions of the theoretical analysis. Highlights of experimental work are presented next.

EXPERIMENTAL STUDIES OF THERMAL AGGLOMERATION

Many experiments have demonstrated a linear relationship between $\frac{1}{n}$ and time in agreement with Eq. (11), even when there is a large change in n (as much as 10 to 30 times) during the time of the experiment. Figure 2 presents some work of Derjaguin and Vlasenko demonstrating this point.[12] Derjaguin and Vlasenko used particles of initial average radii of 0.1 to 0.3 μm and the particles increased in size two to three times during the experiments. Note that times of the order of 100 min were required. This might be expected to produce curvature, and the fact that it does not suggests that the effect of the increase in the average particle size is compensated by the simultaneous increase in polydispersion. According to Fuchs,[4] the smaller the initial radius of the particles the more important becomes the effect of the change in particle size and a linear relationship might not be expected for very small particles. The behavior of ammonium chloride aerosols studied by Whytlaw-Gray and Patterson, shown by Figure 3, may be an example of this effect of size.[13] Both weight and number concentrations are given, and decreasing weight concentrations in general correspond to decreasing particle size. The top curve corresponds to a particle size of about 0.08 μm. The increasing curvature with decreasing size is very marked.

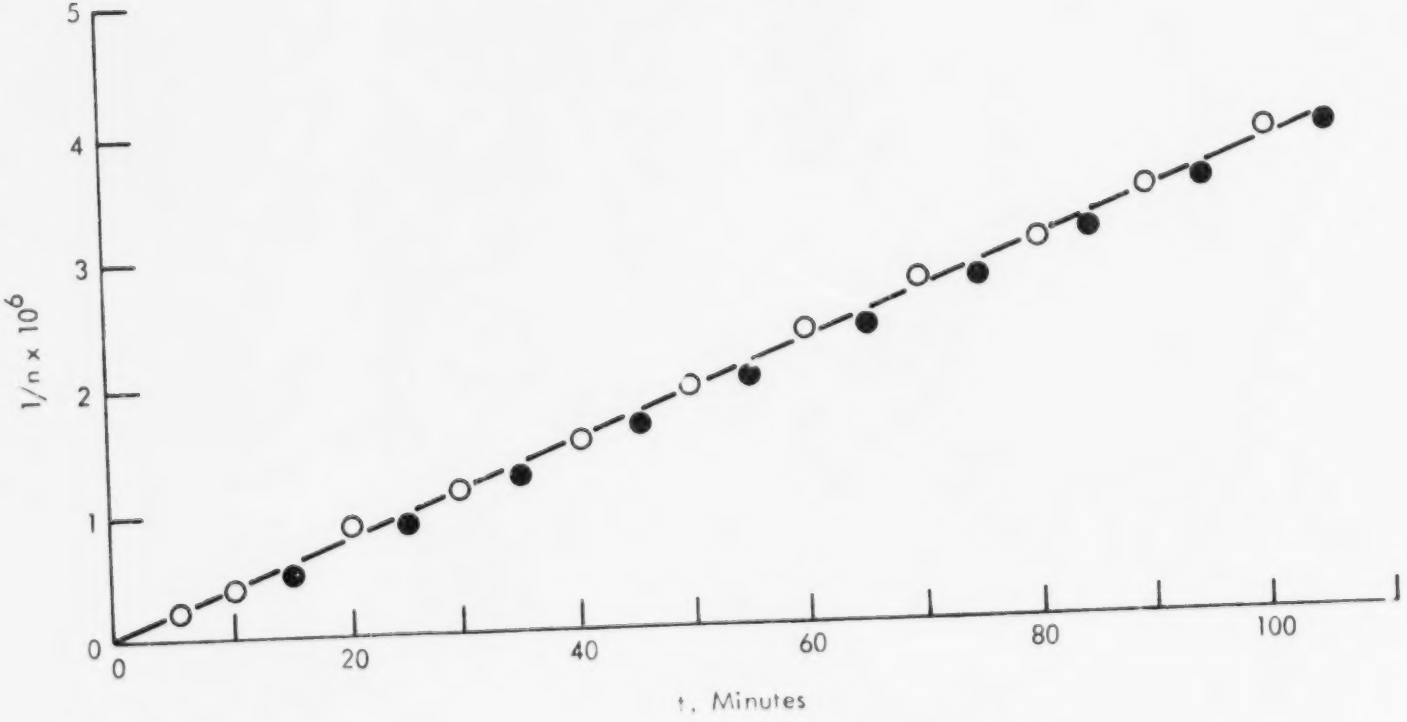

Figure 2. The kinetics of thermal coagulation.

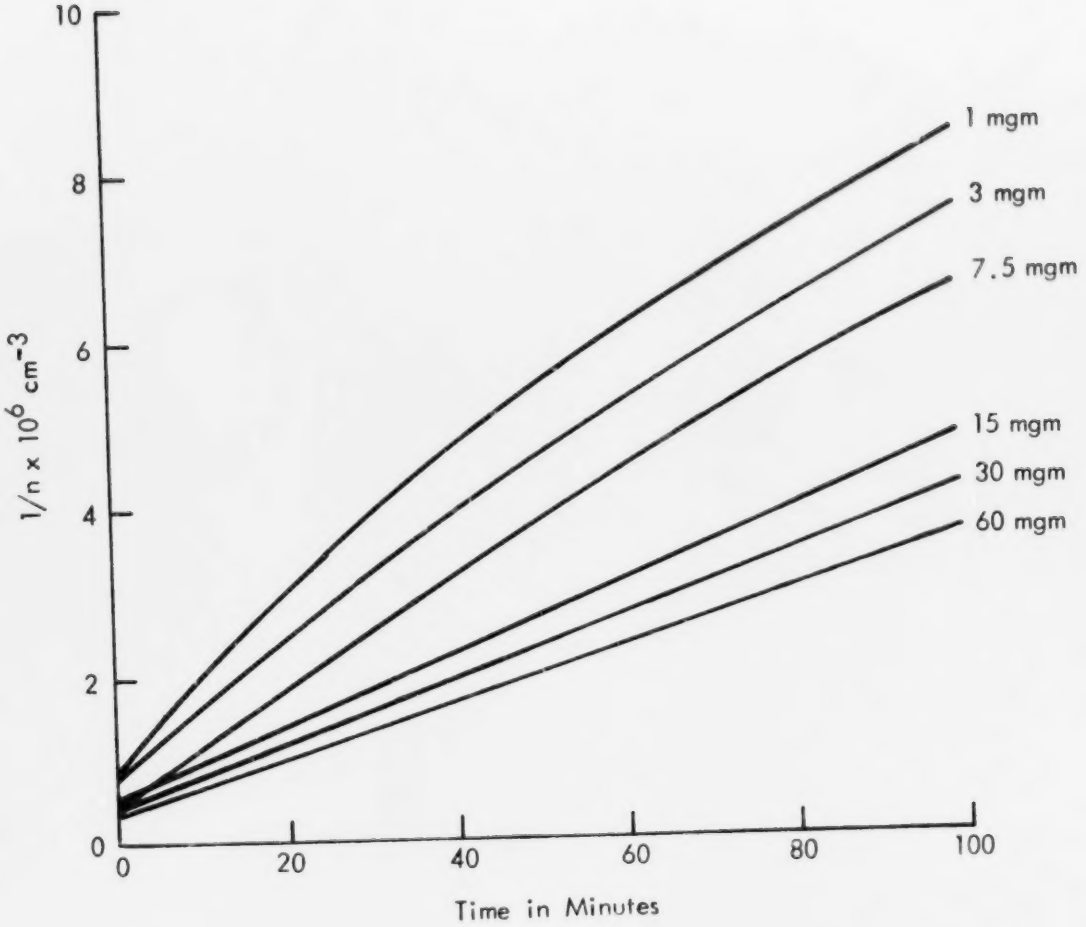

Figure 3. The coagulation of ammonium chloride aerosols.[3]

Table 3 presents some experimentally determined values of coagulation coefficients for several aerosols. The theoretical value shown in Table 3 is for monodisperse aerosols which are large relative to the mean free path of the gas. In this case $K_o = \frac{4kT}{3\eta}$ or in terms of the gas constant $K_o = \frac{4RT}{3N\eta}$ where N is the concentration of particles and η is gas viscosity. The deviation from the theoretical value shown in Table 3 probably results largely from a combination of polydispersity and electrical charging.

Table 3. COAGULATION CONSTANTS FOR SEVERAL AEROSOLS

Dispersed material	$K \times 10^8$ ($cm^3\ min^{-1}$)
Theoretical value	1.8
Stearic acid	3.1
Ammonium chloride	3.0-4.7
Cadmium oxide	4.0-5.3
Magnesium oxide	8.5-10.9
Copal resin	9.3
Carbon	14.1
Zinc oxide	18.9-19.6
Silica powder	26.0-28.0

Experimental evidence also suggests that the more nearly an aerosol approaches monodispersity the more slowly it coagulates. Also, a system with sufficiently narrow size distribution exhibits second, third, and higher modes in the size distribution as coagulation proceeds. The higher modes correspond to the coalescence of two, three, and more particles of the initial modal radius. A polydispersed system does not give rise to higher order modes.

CONCLUSIONS

Both theoretical analyses and experimental studies pinpoint an overriding disadvantage of thermal agglomeration with regard to industrial gas cleaning applications--the long time required to achieve significant particle growth. Residence times of the order of many minutes or even hours are required for significant agglomeration and particle growth to occur via thermal agglomeration. In contrast, industrial gas cleaning applications would require residence times of 10 sec or less.

The main variables which can be used to enhance the rate of thermal agglomeration are particle size and concentration, gas composition and gas temperature. The temperature and gas composition are for the most part not useful variables because they will be a characteristic of the effluent stream from a specific source.

The possibility of influencing the agglomeration rate of particles by introducing a second gas or vapor has been explored in several experimental programs, and the only clear-cut results seem to be those in which the added vapor in some ways affects the shape of the particles, or in which a vapor is actually being transferred between the vapor phase and the particles so that appreciable gaseous diffusion occurs. The latter case is really diffusiophoresis and is not actually thermal agglomeration.

One could alter the agglomeration rate by changing the particle size distribution and concentration by seeding the aerosol with large particulates which act as "agglomeration sites." However, this technique while possibly being effective at an early stage in the agglomeration cycle, would rapidly lose effectiveness because of the n^2 dependence of the agglomeration process. Continuous seeding would be required to maintain the accelerated rate.

Successful utilization of the factors which promote thermal agglomeration is not likely to reduce residence times to anything near those required for industrial applications. Thus, thermal agglomeration is not a viable approach to pursue to augment the ability of control systems to collect fine particulate emissions.

REFERENCES

1. Hidy, G. M., and J. R. Brock, J. Colloid Sci., 20, 477 (1965).

2. Smoluchowski, M. von, Z. Physik. Chem., 92, 129 (1917).

3. Zebel, G., in Aerosol Science, edited by C. N. Davies, Academic Press, New York (1966).

4. Fuchs, N. A., The Mechanics of Aerosols, Pergamon Press, New York (1964).

5. Hidy, G. M., and J. R. Brock, The Dynamics of Aerocolloidal Systems, Vol. 1, Pergamon Press, New York (1970).

6. Müller, H., Kollordzentschrift, 27, 223 (1928).

7. Zebel, G., Kolloid Z, 156, 102 (1958).

8. Schumann, T., Quart. J. Royal Met. Soc., 66, 195 (1940).

9. Todes, O., Symposium on Problems of Kinetics and Catalysis, ONTI, Moscow-Leningrad, 7, 137 (1949).

10. Smoluchowski, M. von, Phys. Z., 17, 557-585 (1916).

11. Smoluchowski, M. von, Z. Phys. Chem., 92, 129 (1918).

12. Derjaguin, B., and G. Vlasenko, Dokl. Akad. Nauk. SSSR, 63, 155 (1948).

13. Whytlaw-Gray, R., and H. S. Patterson, Smoke, Edward Arnold, London (1932).

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